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Davies, Rosalind A.; Anderson, Paul A.

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Short Communication

# Synthesis and characterization of two new amide chloride compounds: Potential $H_2$ storage materials

Rosalind A. Davies [a,b], Paul A. Anderson [a,*]

[a] Hydrogen Storage Chemistry Group, School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

[b] Hydrogen and Fuel Cell Group, School of Chemical Engineering, University of Birmingham, Edgbaston, B15 2TT, United Kingdom

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ABSTRACT

Two new amide chloride phases, with approximate stoichiometries $Li_7(NH_2)_6Cl$ and $Li_6Mg_{0.5}(NH_2)_6Cl$, have been identified by powder X-ray diffraction, and their hydrogen storage properties studied. Both phases released hydrogen on reaction with LiH at a lower temperature than observed for lithium amide, and ammonia release was suppressed. The chloride ions were maintained within the structure after hydrogen desorption and rehydrogenation, raising the possibility that the materials might be cycled. The desorption properties of $Li_7(NH_2)_6Cl$ were found to be similar to the previously reported amide chloride $Li_4(NH_2)_3Cl$ but with a much reduced gravimetric penalty owing to chloride incorporation. Rehydrogenation of the imide products of reaction of both $Li_7(NH_2)_6Cl$ and $Li_6Mg_{0.5}(NH_2)_6Cl$ with LiH occurred more readily at 90 bar and 300 °C than that of $Li_4(NH_2)_3Cl$.


## Introduction

Currently, the majority of electrical and thermal energy is generated by the combustion of fossil fuels: coal, oil and natural gas. This is because they have been easy to mine, transport, store and burn. However, increasing concerns about the security and longevity of their supply and the pollution caused by their combustion are leading to the need for development of alternative technologies [1]. Hydrogen has the potential to form part of a renewable and sustainable energy system as an energy carrier, particularly for automotive applications. This is because it can be produced from renewable sources, stored *via* a variety of methods and then used with only water being emitted at the point of use [2]. Electricity is the main alternative to hydrogen for this purpose, with batteries being used for storage. The dominance of one of these technologies over the other will depend on a number of factors, but for hydrogen to become competitive with batteries, a safe and efficient high capacity storage system needs to be developed.

* *Corresponding author.*
E-mail address: p.a.anderson@bham.ac.uk (P.A. Anderson).
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There are many materials that have been shown to store hydrogen reversibly at higher densities than gaseous or liquid hydrogen. Automotive applications require the material to be light, prompting increasing focus on the complex hydrides of lighter elements such as aluminium (alanates) [3] and boron (borohydrides) [4]. However, although often exhibiting favourable thermodynamics, these materials generally suffer from slow kinetics of hydrogen absorption and/or desorption. Although significant improvements can be seen on addition of transition metal catalysts [3], this problem is far from being resolved.

In comparison, lithium amide, where the hydrogen atoms are instead bound to nitrogen, is more promising in this respect. Although thermal decomposition of $LiNH_2$ alone evolves ammonia rather than hydrogen, addition of lithium hydride creates a pathway that can produce up to 9.3 wt% of hydrogen in two stages (Equation (1)) [5]. However, the second stage of this reaction requires temperatures above 320 °C [6] and is generally not considered to be a viable hydrogen storage reaction.

$$LiNH_2 + 2LiH \leftrightarrow 2Li_2NH + LiH + H_2 \leftrightarrow Li_3N + 2H_2 \quad (1)$$

The addition of $MgH_2$ to $LiNH_2$ forms a storage material that can absorb hydrogen reversibly at 200 °C [7], and the Li–Mg–N–H system has been considered to be very promising as a hydrogen storage medium for practical applications [8].

In earlier work, Anderson et al. [9] found that the addition of lithium halides to lithium amide reduced the temperature of hydrogen release whilst suppressing the release of even trace amounts of ammonia. It was also observed that addition of magnesium halides caused a further reduction in the temperature of hydrogen release. However, the addition of halides reduces the gravimetric hydrogen capacity of the material, which is unfavourable for mobile applications.

In this research, we have used powder X-ray diffraction (XRD) and Raman spectroscopy to identify and characterize two new, lighter amide chloride phases, with lower chloride content. The hydrogen storage potential of these phases was investigated using temperature-programmed desorption (TPD) and rehydrogenation experiments.

## Materials and methods

### *Experimental setup*

Lithium amide (Sigma–Aldrich, 95%) and lithium hydride (Sigma–Aldrich, 95%) were used without further purification. Anhydrous lithium and magnesium chlorides (Sigma–Aldrich, ≥98%) were dried at 300 °C under high vacuum ($1 \times 10^{-6}$ mbar) for 24 h prior to use. All manipulations were performed in a dry argon atmosphere glovebox. Amide chlorides were synthesized by grinding the LiCl and $MgCl_2$ with $LiNH_2$ in the molar ratio of 6 $NH_2^-$:1 $Cl^-$, placing the reaction mixture into a quartz tube and heating under an argon flow (1 bar) at 400 °C (LiCl) and 350 °C ($MgCl_2$) for 12 h. Powder XRD data for phase identification were collected on a Bruker D8 Advance diffractometer in transmission geometry with a Cu-K$\alpha_1$ X-ray source; samples were sealed from the atmosphere between two pieces of amorphous tape. Data for structural investigations were collected on a Siemens D5000 diffractometer in capillary mode with a Cu-K$\alpha_1$ X-ray source; samples were sealed in polyimide capillaries, allowing for long data collection times without degradation. Powder synchrotron XRD data were collected on beamline I11 at the Diamond light source, Oxfordshire; samples were sealed in borosilicate glass capillaries to prevent degradation during transportation and measurement. Diffraction data were analysed using the computer program Topas [10], and structure solution was attempted *via* Rietveld refinement of candidate model structures.

Raman spectra were collected on a Renishaw inVia Raman microscope with 488 nm and 532 nm excitation lasers; samples were sealed inside airtight containers under an argon atmosphere. Temperature-programmed desorption with mass spectrometry (TPD–MS) data were collected using a home built TPD apparatus described previously [11], coupled to a quadrupole mass spectrometer (HPR-20, Hiden Analytical); samples were heated at 2 °C $min^{-1}$ to 400 °C and held at temperature for 1 h before cooling.

## Results and discussion

### *Synthesis of the new amide chlorides*

Lithium amide and lithium chloride were ground together and heated at 400 °C for 12 h according to Equation (2).

$$6\ LiNH_2 + LiCl \rightarrow Li_7(NH_2)_6Cl \quad (2)$$

Powder XRD showed that a new phase had been formed that was indexed to a hexagonal unit cell (a = 9.7367(4) Å, c = 8.9307(3) Å) in space group $R\bar{3}$ (Fig. 1). Fig. 2 shows a schematic representation of the anion arrangement in this new rhombohedral amide chloride.

An equivalent new phase was observed when a similar reaction was carried out with ½$MgCl_2$ replacing LiCl according to Equation (3).

$$6\ LiNH_2 + ½\ MgCl_2 \rightarrow Li_6Mg_{0.5}(NH_2)_6Cl \quad (3)$$

The powder X-ray diffraction pattern of this phase is also shown in Fig. 1, exhibiting slightly larger lattice parameters resulting from the replacement of lithium ions by larger magnesium ions. The structure of the new magnesium-containing phase was similar to that of $Li_7(NH_2)_6Cl$, with a disordered replacement of one seventh of the lithium ions by half as many magnesium ions.

The Raman spectra of these two products (Figure s1) showed that the new phases were amides and did not dehydrogenate to imides during synthesis.

### *Thermal decomposition of the amide chlorides*

Reactions of both $Li_7(NH_2)_6Cl$ and $Li_6Mg_{0.5}(NH_2)_6Cl$ with LiH were carried out, maintaining a 1 ($NH_2^-$): 1 ($H^-$) ratio, and the

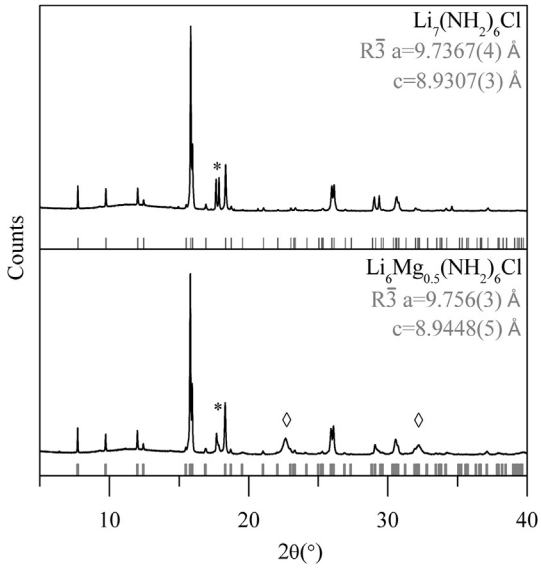


**Fig. 1 – Powder synchrotron XRD patterns of the new amide chlorides; tick marks indicate peak positions for the new phases; stars mark peaks from $Li_2O$ and diamonds those from MgO.**

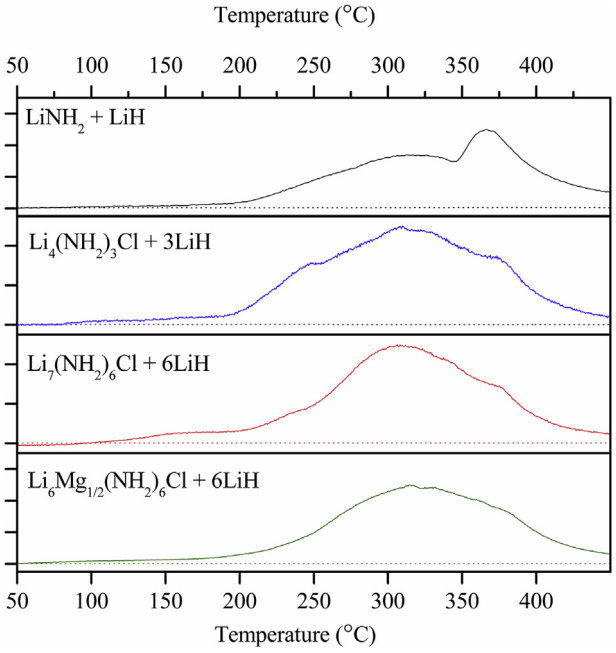


**Fig. 3 – TPD–MS profiles from the reactions of lithium amide and the amide chlorides with LiH for both hydrogen (solid lines) and ammonia (dashed lines).**

normalized hydrogen release profiles are shown in Fig. 3 alongside the profiles for the same reaction for $LiNH_2$ and $Li_4(NH_2)_3Cl$.

For the reaction of $LiNH_2$ and LiH hydrogen release at a low level was observed between 100 and 200 °C before a steady increase in hydrogen desorption from around 210 °C to over 300 °C. This was followed by a second, faster, hydrogen release at 350 °C, ultimately peaking at around 370 °C. This second desorption occurred simultaneously with release of approximately 1.7 mol% of ammonia.

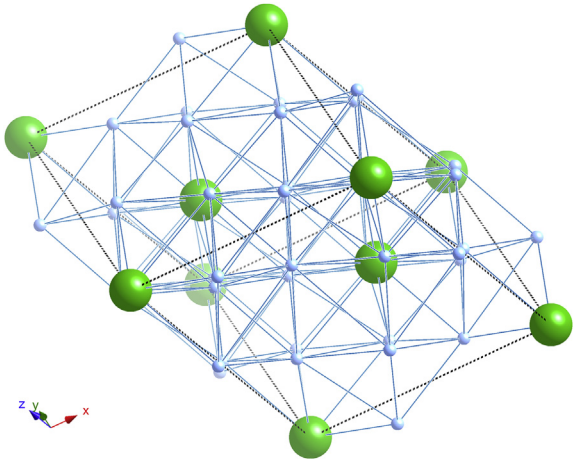

**Fig. 2 – Schematic representation of the anion arrangement in rhombohedral $Li_7(NH_2)_6Cl$ [see also Table s1]. Nitrogen is indicated by blue spheres (small) and chloride by green spheres (large). The unit cell is shown by dotted grey lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)**

For the amide chlorides, the onset of hydrogen release occurred at similar temperatures to that observed for $LiNH_2$ but the rate of release at temperatures below 200 °C was increased in all cases. The desorption profile for $Li_4(NH_2)_3Cl$ showed a broad hydrogen desorption peaking at 320 °C, with shoulders at around 260 °C and 380 °C. The profile of the hydrogen desorption for $Li_7(NH_2)_6Cl$ was almost identical to that for $Li_4(NH_2)_3Cl$ despite the halving of the chloride content. The addition of magnesium had very little effect on the desorption profile, despite previous investigations indicating that the inclusion of magnesium reduces the temperature of hydrogen release [7,12]. This may be because the lithium sites in the $Li_7(NH_2)_6Cl$ structure are not fully occupied, and therefore addition of magnesium and the associated creation of further cation vacancies will not necessarily have a significant effect on the properties. No ammonia was detected above the detection limit of the mass spectrometer for any of the amide chlorides studied, confirming that the doping of lithium amide with chloride suppresses ammonia release.

Powder XRD patterns of the solid products of the reactions of $Li_7(NH_2)_6Cl$ and $Li_6Mg_{0.5}(NH_2)_6Cl$ with LiH are shown in Fig. 4. These patterns closely resemble imide chlorides formed by direct reaction of $Li_2NH$ with LiCl and $MgCl_2$ [9]. Raman spectroscopy (see Figure s2), confirmed that the products are in the imide form, leading to the proposed decomposition reactions shown below in Equations (4) and (5):

$$Li_7(NH_2)_6Cl + 6LiH \rightarrow Li_{13}(NH)_6Cl + 6H_2 \quad (4)$$

$$Li_6Mg_{0.5}(NH_2)_6Cl + 6LiH \rightarrow Li_{12}Mg_{0.5}(NH)_6Cl + 6H_2 \quad (5)$$

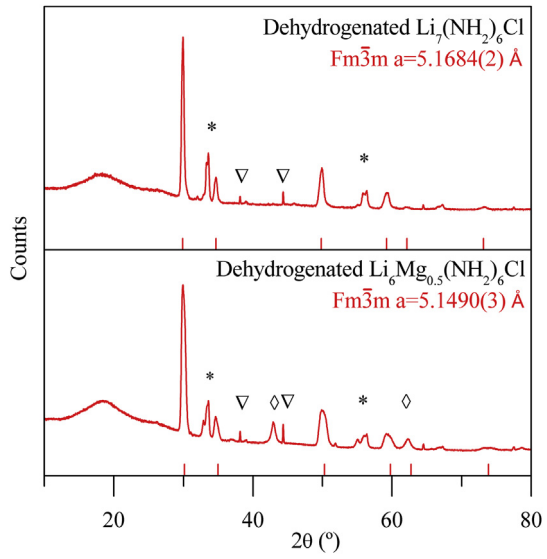


**Fig. 4 – Powder XRD patterns of the dehydrogenation products of the new amide chlorides after reaction with LiH; tick marks indicate peak positions for the dehydrogenated phases; stars mark peaks from $Li_2O$, triangles those for LiH and diamonds those from MgO.**

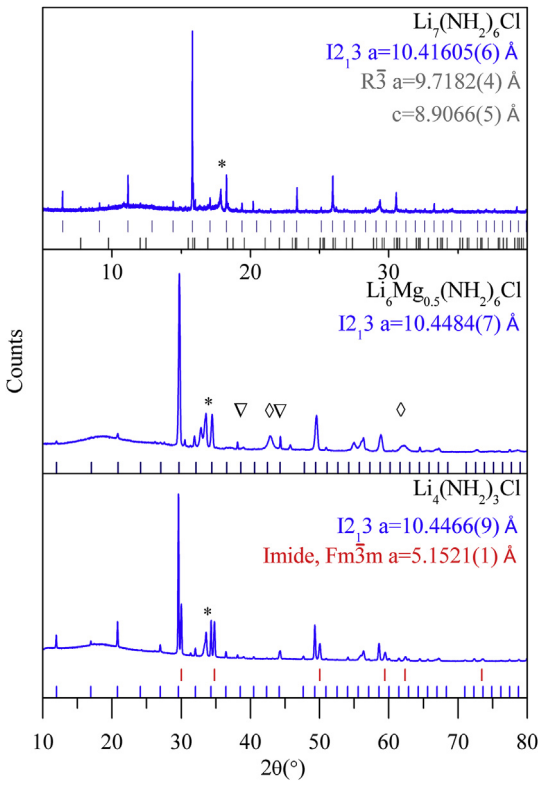


**Fig. 5 – Powder XRD patterns of the rehydrogenation products of the amide chlorides after reaction with LiH; tick marks indicate peak positions for the observed phases [$Li_7(NH_2)_6Cl$: cubic amide chloride (upper ticks), rhombohedral (lower ticks); $Li_6Mg_{0.5}(NH_2)_6Cl$: cubic amide chloride; $Li_4(NH_2)_3Cl$: cubic amide chloride (upper ticks), imide chloride (lower ticks)]; stars mark peaks from $Li_2O$, triangles those from LiH and diamonds those from MgO. [† Synchrotron data for $Li_7(NH_2)_6Cl$.].**

*Rehydrogenation of the imide chlorides*

Once dehydrogenated, the rehydrogenation properties of these new phases were tested using a high pressure hydrogenator under 90 bar $H_2$ for 24 h at 300 °C. The products of rehydrogenation were characterized using Raman spectroscopy (Figure s3), which showed the presence of an amide phase and no imide, confirming that rehydrogenation had taken place.

Powder XRD was used to study the products of rehydrogenation for the two new compounds and $Li_4(NH_2)_3Cl$ after reaction with LiH. It had been previously reported that rehydrogenation of the latter resulted in a hexagonal phase with rhombohedral symmetry [9]. However, in this investigation a cubic phase was formed, and some residual imide was seen to be present, indicating that the rehydrogenation had not gone to completion. In contrast, rehydrogenation of the dehydrogenated forms of $Li_7(NH_2)_6Cl$ and $Li_6Mg_{0.5}(NH_2)_6Cl$ was virtually complete, with the lithium magnesium imide chloride also forming a cubic structure, and the lithium only analogue forming a 4:1 mixture of cubic and rhombohedral phases (Fig. 5).

This difference in structure is also apparent when comparing the Raman spectra of the as-synthesized rhombohedral phases (Figure s1) with those for the rehydrogenated cubic phases (Figure s3). The Raman spectrum for the lithium only phase after rehydrogenation was similar to that observed previously for the cubic $Li_4(NH_2)_3Cl$ [9], but with shoulder peaks representing the small amount of rhombohedral phase present.

## Conclusions

Two new amide chlorides, $Li_7(NH_2)_6Cl$ and $Li_6Mg_{0.5}(NH_2)_6Cl$ have been synthesized that release hydrogen on reaction with LiH. Both new phases showed a reduction in the hydrogen desorption temperature compared to lithium amide and ammonia release was eliminated. Hydrogen desorption properties of both $Li_7(NH_2)_6Cl$ and $Li_6Mg_{0.5}(NH_2)_6Cl$ on reaction with LiH were found to be similar to the previously reported amide chloride $Li_4(NH_2)_3Cl$, but with a much reduced gravimetric penalty owing to chloride incorporation. Hydrogen release was also found to be reversible for both new compounds, with rehydrogenation going to completion. This is an improvement when compared to $Li_4(NH_2)_3Cl$, where residual imide was observed in the diffraction pattern of the product of rehydrogenation under identical conditions.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2014.12.044.

## REFERENCES

[1] Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, et al. IPCC: summary for policymakers. 2007.
[2] Armstrong F, Blundell K. Energy beyond oil. Oxford University Press; 2007.
[3] Bogdanović B, Schwickardi M. Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials. J Alloys Comp 1997;253–254:1–9.
[4] Züttel A, Rentsch S, Fischer P, Wenger P, Sudan P, Mauron P, et al. Hydrogen storage properties of $LiBH_4$. J Alloys Comp 2003;356–357:515–20.
[5] Chen P, Xiong Z, Luo J, Lin J, Lee Tan K. Interaction of hydrogen with metal nitrides and imides. Nature 2002;420:302–4.
[6] Chen P, Xiong Z, Luo J, Lin J, Lee Tan K. Interaction between lithium amide and lithium hydride. J Phys Chem B 2003;107:10967–70.
[7] Luo W. ($LiNH_2$–$MgH_2$): a viable hydrogen storage system. J Alloys Comp 2004;381:284–7.
[8] Liang C, Liu Y, Fu H, Ding Y, Gao M, Pan H. Li-Mg-N-H-based combination systems for hydrogen storage. J Alloys Comp 2011;509:7844–53.
[9] Anderson PA, Chater PA, Hewett DR, Slater PR. Hydrogen storage and ionic mobility in amide halide systems. Faraday Discuss 2011;151:271.
[10] Coelho AA. TOPAS academic v4.1, general profile and structure analysis software for powder diffraction data. Brisbane. 2007.
[11] Chater PA, Anderson PA, Prendergast JW, Walton A, Mann VSJ, Book D, et al. Synthesis and characterization of amide–borohydrides: new complex light hydrides for potential hydrogen storage. J Alloys Comp 2007;446–447:350–4.
[12] Leng HY, Ichikawa T, Hino S, Hanada N, Isobe S, Fujii H. New metal–N–H system composed of $Mg(NH_2)_2$ and LiH for hydrogen storage. J Phys Chem B 2004;108:8763–5.